

# Real-Time Evolution of the Electron Clouds of Transition Metal Ions: Electron-Pairing Medium of Unconventional High Temperature Superconductors

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## Abstract

The electron-pairing mechanism in unconventional high temperature superconductors (HTS) has not been resolved. The author proposed that the electron-pairing medium of unconventional HTS is the change of the electron clouds of transition metal ions, which is analogous to the lattice vibration in conventional superconductors. Real-time evolution of the electron clouds of transition metal ions under excitations in  $\text{La}_2\text{Fe}_2\text{As}_2\text{O}_2$ , FeSe sheet,  $\text{Fe}_2\text{KSe}_2$ ,  $\text{CaCuO}_2$ , and  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$  was calculated by the time-dependent density functional theory (TDDFT). The characteristic frequency is about 90-250 meV, which is equivalent to the lattice vibration frequencies, showing that the change of the electron clouds of the transition metal ions can be the electron-pairing medium in unconventional HTS.

## 1. Introduction

The discovery of copper-oxide <sup>[1][2]</sup> and iron-based superconductors <sup>[3][4]</sup> indicates that electron-lattice interactions cannot explain the electron-pairing mechanism in unconventional HTS. According to the BCS theory <sup>[5][6]</sup>, the superconducting transition temperature ( $T_c$ ) caused by electron-lattice interactions (at normal pressures) cannot be higher than 40K. The pairing mechanism for unconventional HTS is still under debate. Mr. Anderson <sup>[7]</sup> has raised an important question in 2007: Is There Glue in Cuprate Superconductors? The author believes that, if a medium does exist in unconventional HTS, the medium should change under excitations and the characteristic frequency should be close to that of the lattice

vibrations. Table 1 gives the maximum phonon frequencies and  $T_c$  of three typical conventional superconductors. It is reasonable to guess that the characteristic frequency of the electron-pairing medium in unconventional HTS should be about 100-200 meV. A higher frequency gives a higher  $T_c$ . If the frequency is too low or too high, it is unlikely to be an electron-pairing medium in HTS

Table 1 Maximum phonon frequencies and  $T_c$  of three typical conventional superconductors.

	Pb <sup>[8]</sup>	MgB <sub>2</sub> <sup>[8]</sup>	H <sub>3</sub> S <sup>[9]</sup>
$\omega$ / meV	9	90	250
$T_c$ / K	7	39	164

Based on the above consideration, the author has studied eight typical unconventional superconductors (Fe<sub>2</sub>KSe<sub>2</sub>, La<sub>2</sub>Fe<sub>2</sub>As<sub>2</sub>O<sub>2</sub>, Nd<sub>2</sub>Fe<sub>2</sub>As<sub>2</sub>O<sub>2</sub>, Ba<sub>2</sub>Fe<sub>4</sub>As<sub>4</sub>, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>9</sub>, Tl<sub>2</sub>Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> and Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub>)<sup>[10]</sup>. Under a static electric field, the electron clouds of transition metal ions change significantly. The author suggests that the change of the electron clouds of transition metal ions may be a new electron-pairing medium. The pairing mechanism is as follows. When a free electron comes to a new place, the electron clouds of the neighboring transition metal ions will change. In this way, the charge densities around the free electron will decrease. When the free electron leaves, the electron clouds of the transition metal ions will not relax immediately, so that there will be a region lack of charge. Another free electron will be attracted. An attraction appears. This mechanism is essentially the same as the electron-lattice interaction, except that the medium is the change of the electron clouds, not the displacement of the ions.

Based on the previous studies, the author has made a further investigation, exploring the frequencies of the change of the electron clouds of transition metal ions. The real-time evolution of charge densities under some excitation of La<sub>2</sub>Fe<sub>2</sub>As<sub>2</sub>O<sub>2</sub>, FeSe sheet, Fe<sub>2</sub>KSe<sub>2</sub>, CaCuO<sub>2</sub> and HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8</sub> has been calculated by TDDFT<sup>[11][12]</sup> method. This paper will report the methods and results.

## 2. Methods

Calculations were conducted within the Octopus package <sup>[13][14][15]</sup>. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used to describe the exchange-correlation energy. The GGA+U method <sup>[16][17]</sup> was taking into account to deal with the strong correlation of the 3d electrons. HSCV pseudopotentials <sup>[18]</sup> were adopted. Approximated Enforced Time-Reversal Symmetry (AETRS) algorithm was used to approximate the evolution operator and the time step is 0.002  $\hbar/\text{eV}$ .

## 3. Results and Discussions

### 3.1 $\text{La}_2\text{Fe}_2\text{As}_2\text{O}_2$

The  $k$ -point setting is  $4 \times 4 \times 2$  and  $5p^6d^16s^2$  of La,  $3p^6d^64s^2$  of Fe,  $3d^{10}4s^2p^3$  of As and  $2s^2p^4$  of O are taken as valence electrons in the calculation. The change of charge densities is induced by a time-dependent electric field:

$$f(t) = F_0 \cos\left(\frac{\pi}{2} \frac{t - 2\tau_0 - t_0}{\tau_0}\right) \cos \omega t \quad \text{If } |t - t_0| > \tau_0, \text{ then } f(t) = 0.$$

where  $F_0 = 1.0 \text{ eV/\AA}$ ,  $\omega = 1.8 \text{ eV}$ ,  $\tau_0 = 5.0/\text{eV}$  and  $t_0 = 5.0/\text{eV}$ . The excitation vanishes after 5000 steps and the charge densities vibrate freely thereafter. After 8000 steps, the charge densities are recorded. Fig. 1 shows the crystal structure and the real-time evolution of the charge density. 100 represents the charge density difference of the 8100th step and that of the 8000th step and the same below. The change of the electron clouds of the Fe ions become obvious gradually with the evolution steps. After 100 steps, almost no change can be seen, and after 500 steps, the change has been obvious. The charge density change reaches its maximum value after 800 steps, and the corresponding time is 1.6  $\hbar/\text{eV}$ . It is the time from zero to the maximum. The time of one period should be  $4 \times 1.6 \hbar/\text{eV}$  and the frequency is about 160 meV. The frequency given in this way is not very accurate and may have an error as large as  $\pm 20\%$ , but the frequency is consistent with the author's guess, indicating that it can be the electron-pairing medium in HTS.

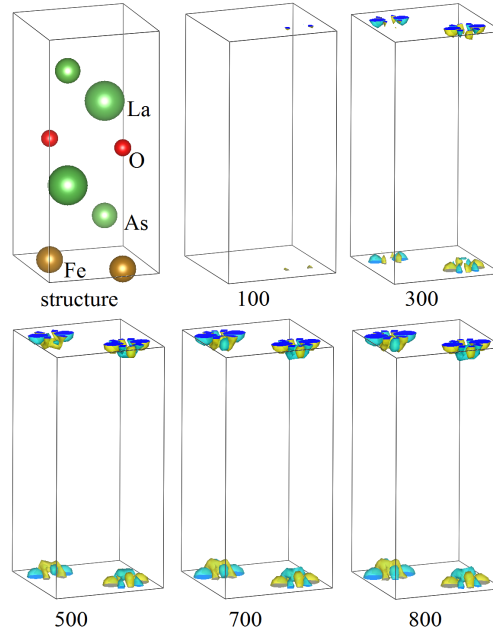


Fig.1 Crystal structure and the charge density evolution of  $\text{La}_2\text{Fe}_2\text{As}_2\text{O}_2$ . The isosurface is  $0.02 \text{ num\_electron/bohr}^3$ . The yellow color represents an increase of the charge density, while the blue a decrease (the same below).

### 3.2 FeSe Sheet<sup>[19]</sup>

$3p^6d^64s^2$  of Fe and  $4s^2p^4$  of Se are taken as valence electrons. A  $4 \times 4 \times 1$   $k$ -point setting was used and the excitation is the same as above. Fig. 2 shows the results. By careful examination, it can be found that the charge density change first increased and then decreased, and then increased again. To give a better illustration, Fig. 3 shows the maximum value of the charge density change as a function of the evolution steps. There are two maximum values: after 550 steps and after 1400 steps. There may be two modes in the evolution. This can also be seen from the shapes the charge density changes after 600 steps and after 1400 steps. The frequencies are approximately 230 meV and 90 meV, respectively.

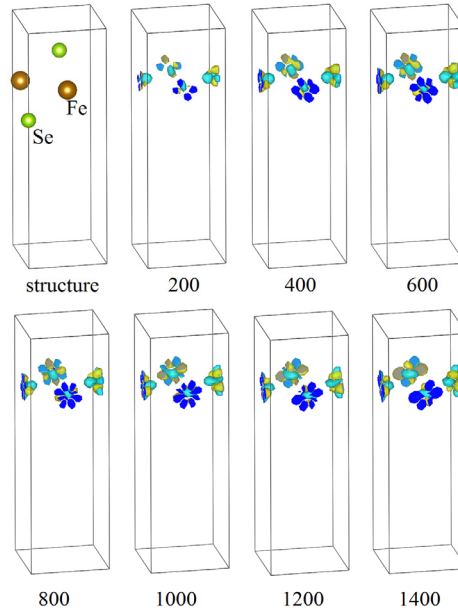


Fig.2 Crystal structure and the charge density evolution of FeSe sheet. The isosurface is 0.01.

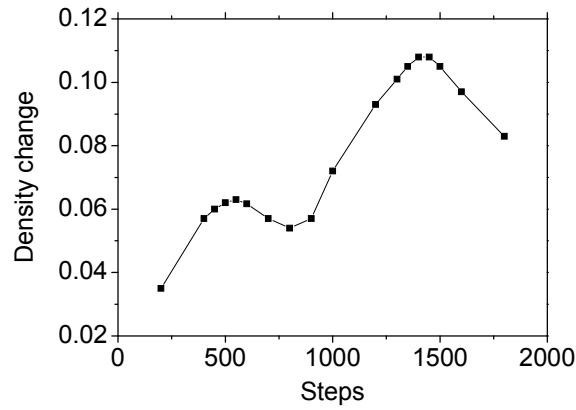


Fig.3 FeSe sheet: The relationship between the maximum value of charge density change and the evolution steps

### 3.3 $K_2Fe_4Se_4-2e$

Two valence electrons were subtracted from  $K_2Fe_4Se_4$  and the valence state of K is +1, Se is -2, and Fe is +2. The excitation is the same as above. There are also two modes in  $K_2Fe_4Se_4-2e$ . Fig. 4 shows the results obtained with a  $k$ -point setting of  $2 \times 2 \times 1$ . The maximum of the charge density change is after 500 steps, and the frequency is approximately 250 meV. Fig. 5 shows the results with a  $k$ -point setting of  $4 \times 4 \times 2$ . The change reaches its maximum after 1100 steps, and the frequency is approximately 100 meV. The difference between the two modes can be seen from the patterns of the charge density changes. Different  $k$ -point settings may lead to different

modes, which needs further investigation.

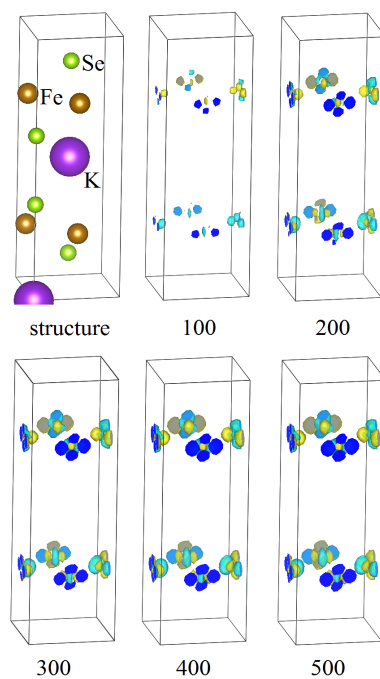


Fig. 4 Crystal structure and evolution of the charge density of  $\text{K}_2\text{Fe}_4\text{Se}_4\text{-2e}$ . The  $k$ -point is set to  $2 \times 2 \times 1$  and the isosurface is 0.04.

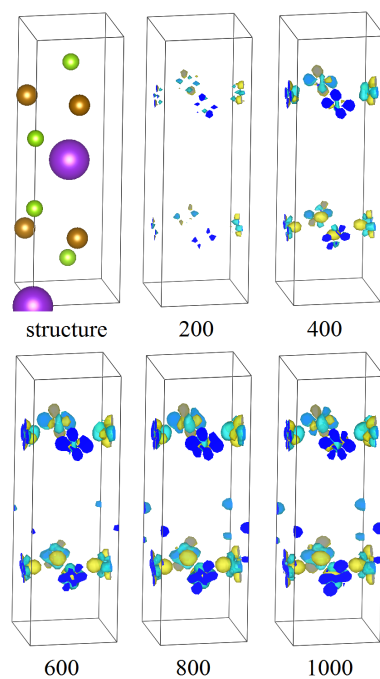


Fig.5 Crystal structure and evolution of the charge density of  $\text{K}_2\text{Fe}_4\text{Se}_4\text{-2e}$ . The  $k$ -point is set to  $4 \times 4 \times 2$  and the isosurface is 0.01.

### 3.4 $\text{CaCuO}_2$ [20]

$5p^6d^{10}6s^2$  of Hg,  $5p^66s^2$  of Ba,  $3p^64s^2$  of Ca,  $3p^6d^{10}4s^1$  of Cu and  $2s^2p^4$  of O are taken as valence electrons. To excite the charge vibration, the position of a Ca atom is slightly changed. The original coordinate is (0, 0.5, 0.5), and modified to (0.02, 0.52, 0.5), ie., the Ca atom was moved in the (001) direction by 0.15 Å. Ground state was calculated. Then the coordinate was modified back to (0,0.5,0.5) for TDDFT calculation. Charge densities were recorded after 13000 steps. Fig. 4 shows the results. The electron cloud of the center Cu ion marked by an arrow changes gradually. The change reaches its maximum value after 1300 steps and the frequency is about 100 meV.

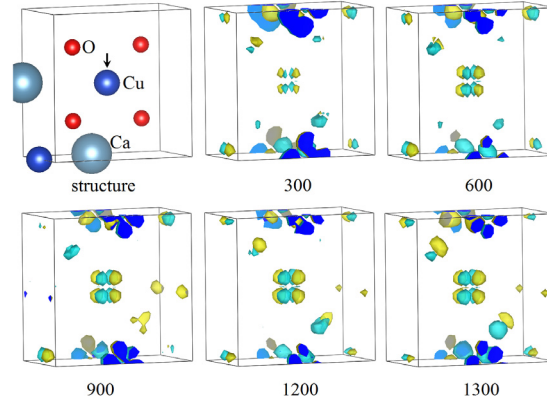


Fig.6 Crystal structure and evolution of the charge density of  $\text{CaCuO}_2$ . The  $k$ -point is set to  $4 \times 4 \times 2$  and the isosurface is 0.03

### 3.5 $(\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8)_2$

The  $k$ -point is set to  $2 \times 2 \times 1$  and vibrations of the charge densities were excited in two ways. Fig. 7 shows the results excited by a time dependent electric field. Charge densities were recorded after 8000 steps. Except Ca ions, the electron clouds of other ions changed obviously. It is worth noting that the oxygen ions in the copper-oxide plane undergo obvious changes. The change in the charge densities of almost all the ions is maximized after 500 steps with a frequency of approximately 250 meV.

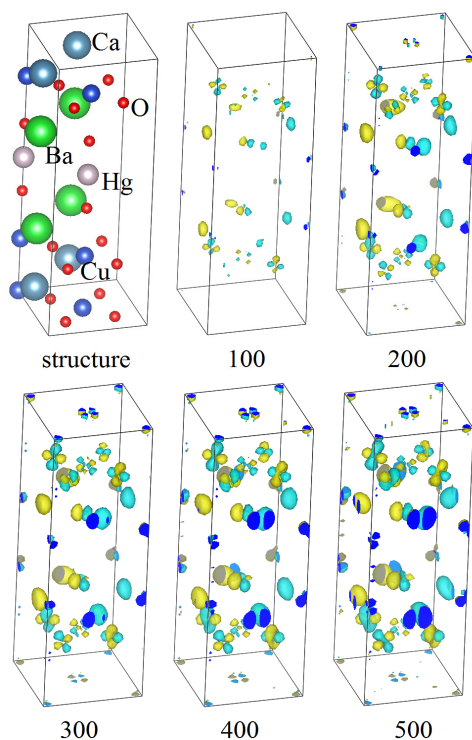


Fig. 7 Crystal structure and evolution of the charge density of  $(\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8)$  excited by a time dependent electric field. The isosurface is 0.005.

Fig. 8 shows the results excited by a slight change in the position of an O atom. The original coordinate of the O ion in the copper oxide plane is  $(0.75, 0.25, 0.0)$ , and modified to  $(0.8, 0.3, 0.0)$ , which is equivalent to a change of about  $0.4 \text{ \AA}$  along the  $(110)$  direction. The ground state was calculated. Then modify the coordinate back to  $(0.75, 0.25, 0.0)$  and conduct TDDFT calculations. After 14000 steps, charge densities were recorded. The change of the electron cloud of the Cu ion indicated by the arrow reaches its maximum after 500 steps. The frequency is approximately  $250 \text{ meV}$ .



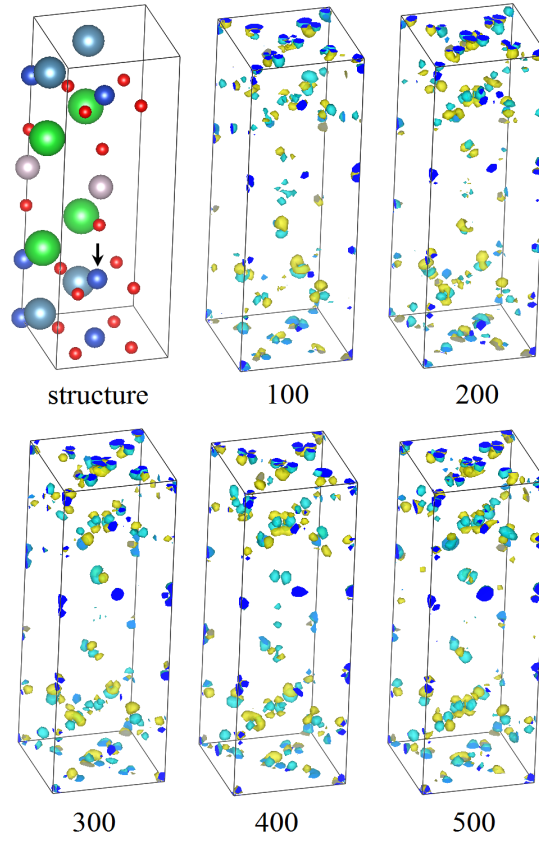


Fig.8 Crystal structure and evolution of the charge density of  $(\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8)$  excited by changing an O atom. The isosurface is 0.05.

#### 4. Conclusion and research prospects

Real-time evolution of the electron clouds of transition metal ions in unconventional HTS was calculated by the TDDFT method. The frequencies of evolution of electron clouds are about 90-250 meV, matching fairly well with the frequencies of the lattice vibrations at normal and high pressures. Though the frequencies obtained by this method are not accurate, it can give a significant evidence that the change of electron clouds can be the electron-pairing medium in HTS. It is worth noting that there are different modes of the change of the electron clouds of the transition metal ions, corresponding to different frequencies. Moreover, the electron clouds have very high frequency vibrations, and the author observed the vibration with lowest frequency.

Why do the electron clouds of transition metal ions change this way? The main reason is that the  $3d$  shell of transition metal ions is not fully filled. The electron

clouds possess no spherical symmetry, and easy to change under electric fields. Furthermore, for an ion with an incompletely shell, such as O ions in copper-oxide planes, same behaviors may occur.

If the change of the electron clouds of transition metal ions is indeed the pairing medium, superconductivity can be divided into two categories according to the pairing medium: “displacement of ions” and “electron cloud change of ions”.

The research of this paper is still incomplete. First, the frequencies should be calculated accurately. Second, experimental results must be given; Third, theoretical calculation of the  $T_c$  of unconventional HTS should be achieved.

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